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In Search of Metal-Metal Metathesis in the
Chemistry of Compounds Containing Metal-To-Metal
Triple Bonds Between Molybdenum
and Tungsten Atoms

by M. H. Chisholm, F. A. Cotton
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in solution at 80°C or at 25°C in the presence of U.V. irradiation.
The mechanism leading to this metathesis is unknown.

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In Search of Metal-Metal Metathesis in the
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and Tungsten Atoms

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Introduction

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→ The occurrence of transition metal complexes containing metal-to-metal multiple bonds is now well documented.¹ Scores of such compounds have been structurally characterized and several have been subjected to detailed spectroscopic examination. Recently X_{α} -SW calculations have been carried out on compounds containing M-M bonds of order 3² and 4³⁻⁵ and the results have been correlated with the observed spectroscopic data. Despite the emergence of a basic understanding of the electronic structure of these compounds little is known about (i) the mechanisms of their formation and (ii) the relationships that exist between the formation/existence of dinuclear compounds with M-M multiple bonds and cluster or polynuclear compounds of the same empirical formula.

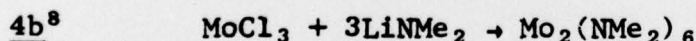
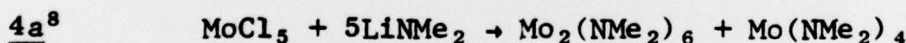
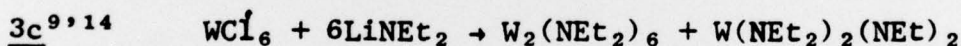
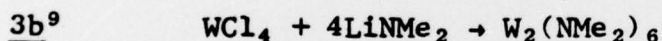
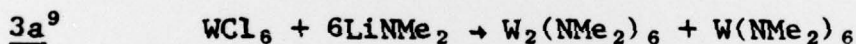
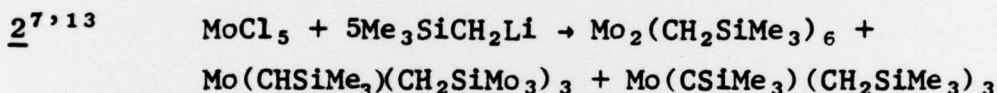
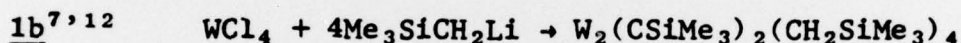
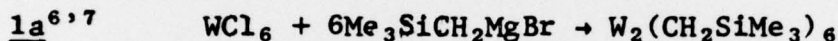
We have sought to gain insight into some of these mystiques by looking for the formation of heterodinuclear compounds containing M-Mⁿ multiple bonds. We report here some findings relating to compounds containing triple bonds between molybdenum and tungsten atoms.

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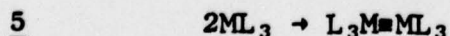
Results and Discussion

M₂L₆ Compounds (M=Mo,W; L=R(alkyl),NR₂)

Recent work has established a structurally related series of compounds of general formula M₂L₆, where M=Mo and W and L = R (β-elimination stabilized alkyl)^{6,7}, NR₂^{8,9} and OR^{10,11}. The alkyls and dialkylamides are formed in metathetic reactions represented by 1 through 4 below; the alkoxides are formed by alcoholysis reactions involving the dialkylamides.

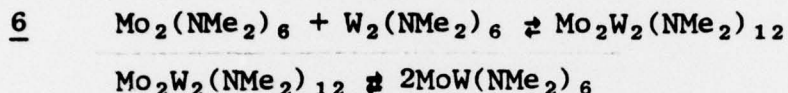


The nature of these reactions (1 through 4 above) is clearly complex. It has been suggested¹⁵ that the dinuclear compounds might arise from the coupling of two reactive mononuclear species, eq. 5.



In an attempt to ascertain whether 5 might be operative we reacted a finely divided mixture of WCl₆ and MoCl₅ with LiNMe₂ and analyzed the crystalline dimethylamides obtained from

this reaction by mass spectroscopy. No heterodinuclear ion $\text{MoW}(\text{NMe}_2)_6^+$ was observed; nor were any other MoW dinuclear ions detected.¹⁶ (The mass spectrum was a superimposition of those obtained for the pure compounds $\text{Mo}_2(\text{NMe}_2)_6$, $\text{W}_2(\text{NMe}_2)_6$ and $\text{W}(\text{NMe}_2)_6$) This observation by no means rules out a coupling reaction, reaction 5, but it does indicate that neither the microscopic reverse of 5 (involving M-M bond rupture) nor a reversible association reaction 6 are operative.



Further support of this conclusion is seen in the following. In two separate experiments equimolar amounts of $\text{Mo}_2(\text{NMe}_2)_6$ and $\text{W}_2(\text{NMe}_2)_6$ were dissolved in toluene and placed in sealed tubes. One tube was heated to 80°C for 24 hr; the other was exposed to U.V. irradiation at 25°C for 24 hr. The tubes were then opened, the solvent stripped off and the solids were analyzed by mass spectroscopy. No MoW-containing ions were observed. (The mass spectrum was merely a superimposition of those obtained for the pure compounds $\text{Mo}_2(\text{NMe}_2)_6$ and $\text{W}_2(\text{NMe}_2)_6$).

It could be argued that formation of $\text{MoW}(\text{NMe}_2)_6$, either by the microscopic reverse of 5 or by an associative process such as 6, was not favored due to thermodynamic factors. Consequently, we set out to make $\text{MoW}(\text{NMe}_2)_6$. We reacted $\text{Mo}(\text{CO})_6$ (1 equiv) with WCl_6 (2 equiv) and obtained a halide of empirical composition $\text{MoW}_2\text{Cl}_{12}$. (the analogous reaction $\text{W}(\text{CO})_6$ (1 equiv) + WCl_6 (2 equiv) yields WCl_4 ¹⁷). The mixed metal halide was then reacted with LiNMe_2 and the crystalline dimethylamides obtained were analyzed by mass spectroscopy. Ions corresponding to $\text{Mo}_2(\text{NMe}_2)_6^+$, $\text{MoW}(\text{NMe}_2)_6^+$ and $\text{W}_2(\text{NMe}_2)_6^+$ were detected in the approximate intensity ratio 1:2:2 respectively. Although this ratio of intensities need have no correlation with the thermodynamic equilibrium of the species present, it does show that M-M¹ metathesis reactions involving either the microscopic reverse of 5 or associative reactions of the type 6 are not kinetically facile.

This conclusion is further supported by our observation that when $W_2(NMe_2)_6$ and the perdeutero compound $W_2(NMe_2)_6-d_{36}$ were allowed to react both thermally and photochemically, only $W_2(NMe_2)_6^+$ and $W_2(NMe_2)_6-d_{36}^+$ ions were detected. No ions corresponding to ligand exchange i.e., $W_2(NMe_2)_x(N(CD_3)_2)_{6-x}$ were detected.

In similar experiments $Mo_2(CH_2SiMe_3)_6$ and $W_2(CH_2SiMe_3)_6$ were mixed together in toluene. Neither heating to $80^\circ C$, nor exposure to U.V irradiation for 24 hr led to formation of $MoW(CH_2SiMe_3)_6$, or at least, no ion corresponding to $MoW(CH_2SiMe_3)_6^+$ was found in the mass spectrum of the resulting solids. However, a considerable degree of decomposition occurred in these reactions since the tungsten compound is thermally and photochemically sensitive. The decomposition products were not characterized.

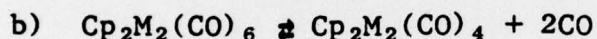
$Cp_2M_2(CO)_4$ Compounds (M=Mo and W)

On the basis of short M-M distances and attainment by the metal atoms of an 18 valence shell of electrons, the compounds $Cp_2M_2(CO)_4$, where M=Mo or W, may be considered to have M-M triple bonds¹⁸. These compounds have been shown to add acetylenes,^{18,19} allenes^{20,21} and other unsaturated²² molecules on to form adducts $Cp_2M_2(CO)_4(un)$, in which the unsaturated group adds across the M-M bond. Evidence has been presented to support the view that this addition involves the direct interaction of the dinuclear compound and the unsaturated organic substrate: mononuclear species are not involved in adduct formation²¹. It seemed plausible that these compounds ($Cp_2M_2(CO)_4$) might be capable of showing M-M metathesis reactions by a reversible associative reaction sequence akin to that shown in eq. 6.

In separate experiments $Cp_2Mo_2(CO)_4$ and $Cp_2W_2(CO)_4$ were allowed to react in toluene for 24 hr (i) at room temperature,

(ii) at 80°C and (iii) at 20°C in the presence of U.V. irradiation. Subsequently, the solvent was stripped and the resulting solids analyzed by mass spectroscopy. The room temperature reaction gave rise to ions derived from the respective homodinuclear species. However, in both the thermal reaction at 80°C and photochemical reaction heterodinuclear ions derived from $\text{Cp}_2\text{MoW}(\text{CO})_4$ were observed in the mass spectra.

In these reactions M-M metathesis could occur as a result of either an associative or dissociative process. However, a CO catalyzed mechanism could also be operative. See 7 below



It is difficult to remove all traces of $\text{Cp}_2\text{M}_2(\text{CO})_6$ compounds from solutions of the dinuclear tetracarbonyls because (i) the equilibrium 7b lies well to the left and (ii) thermal or photochemical decomposition of $\text{Cp}_2\text{M}_2(\text{CO})_4$ compounds liberates CO.

Conclusions

M-M metathesis reactions may be used as mechanistic probes in the chemistry of compounds containing M-M multiple bonds.

1) $\text{M}_2(\text{NMe}_2)_6$ compounds (M=Mo,W) are not formed by the coupling of two reactive mononuclear species, $\text{M}(\text{NMe}_2)_3$.

2) $\text{M}_2(\text{NMe}_2)_6$ compounds (M=Mo,W) are not labile toward M-M bond cleavage or associative reactions which lead to M-M metathesis.

3) $\text{Cp}_2\text{M}_2(\text{CO})_4$ compounds (M=Mo,W) readily undergo M-M¹ metathesis in solution at 80°C or at 25°C in the presence of U.V. irradiation. The mechanism leading to metathesis remains to be established.

Experimental Section

General procedures have been described previously.⁸

$\text{Mo}_2(\text{NMe}_2)_6$,⁸ $\text{W}_2(\text{NMe}_2)_6$,⁹ $\text{W}_2(\text{NMe}_2)_6\text{-d}_{36}$,⁹ $\text{Mo}_2(\text{CH}_2\text{SiMe}_3)_6$,⁶ $\text{W}_2(\text{CH}_2\text{SiMe}_3)_6$,⁷ $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ ¹⁸ and $\text{Cp}_2\text{W}_2(\text{CO})_4$ ²³ were prepared according to methods described in the literature.

Mass spectra were obtained from an AEI MS9 mass spectrometer by the method of direct insertion (90-120°C).

$\text{Cp}_2\text{Mo}_2(\text{CO})_4 + \text{Cp}_2\text{W}_2(\text{CO})_4$

a) At room temperature: $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ (0.3g) and $\text{Cp}_2\text{W}_2(\text{CO})_4$ (0.4g) were dissolved in toluene (2 mL) in a round bottomed flask (100 mL) under an atmosphere of dry and oxygen free nitrogen. This solution was stirred magnetically for 12 hr. The solvent was then stripped off and the solids analyzed by mass spectroscopy. No MoW-containing ions were observed. The spectrum was merely a superimposition of those obtained for $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ and $\text{Cp}_2\text{W}_2(\text{CO})_4$.

b) 25°C, 12 hr: $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ and $\text{Cp}_2\text{W}_2(\text{CO})_4$ were dissolved in toluene as in (a) above. The solution was then kept at ca. room temperature (25°C) by rapid air-cooling while U.V. irradiation from a GE275 watt sunlamp was directed at flask for 12 hr. The solids obtained after stripping the solvent were analyzed by mass spectroscopy. MoW-containing ions were present, in particular $\text{Cp}_2\text{MoW}(\text{CO})_4^+$ and Cp_2MW^+ . The relative intensities of Mo_2^+ , MoW^+ and W_2^+ containing ions was ca. 1:2:1.

c) 120°C, 12 hr: $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ and $\text{Cp}_2\text{W}_2(\text{CO})_4$ were dissolved in m-xylene (20 mL) as in (a) above. The solution was heated in an oil bath and maintained at ca. 120°C (reflux) for 24 hr. The solid obtained after stripping the solvent was analyzed by mass spectroscopy. The mass spectrum was virtually identical to that obtained in (b) above.

$\text{Mo}_2(\text{NMe}_2)_6 + \text{W}_2(\text{NMe}_2)_6$; $\text{W}_2(\text{NMe}_2)_6 + \text{W}_2(\text{NMe}_2)_6\text{-d}_{36}$

Equimolar quantities of the appropriate dimethylamides were dissolved in toluene as above and either heated to 80°C in an

oil bath, or maintained at ca. room temperature and exposed to U.V. irradiation for 12 hr. The solids obtained after stripping the solvent were analyzed by mass spectroscopy. The spectra corresponded to a superimposition of the spectra obtained for $\text{Mo}_2(\text{NMe}_2)_6$ and $\text{W}_2(\text{NMe}_2)_6$. No MoW-containing ions were observed.

$\text{Mo}_2(\text{CH}_2\text{SiMe}_3)_6 + \text{W}_2(\text{CH}_2\text{SiMe}_3)_6$

Equimolar quantities of $\text{Mo}_2(\text{CH}_2\text{SiMe}_3)_6$ and $\text{W}_2(\text{CH}_2\text{SiMe}_3)_6$ were dissolved in toluene and reacted thermally and photochemically as above. No MoW-containing ions were detected in the mass spectrum of the resulting solids.

Preparation of the tungsten-molybdenum chloride or empirical formula ' $\text{MoW}_2\text{Cl}_{12}$ ' .

WCl_6 (28.03g; 70.68 mmol) was added to $\text{Mo}(\text{CO})_6$ (9.33g; 35.34 mmol) in a 500 ml flask. A reaction appeared to take place between the two solids and on addition of chlorobenzene (50 ml) a vigorous, but smooth, reaction occurred with gas evolution. After 12 hr, a brown solid had formed and the reaction mixture was then refluxed for a further 3 hr. Removal of solvent gave 29.15 g of a black solid (92.8% yield based on ' $\text{MoW}_2\text{Cl}_{12}$ '), which did not show any evidence of residual CO ligands in the infrared spectrum. The product was used without further purification and is assigned the empirical formula " $\text{MoW}_2\text{Cl}_{12}$ " based on the following analytical data: Found (calcd) Mo (10.79); W (41.36); Cl (47.85).

Reaction of ' $\text{MoW}_2\text{Cl}_{12}$ ' with LiNMe_2 .

LiNMe_2 was generated by the addition of HNMe_2 (142.1 mmol) to BuLi (142.1 mmol) in hexane (62 mL) at -80°C . The reaction mixture was allowed to warm to room temperature and then diethyl ether (100 mL) was added to give a slurry of white LiNMe_2 . The slurry was then cooled to 0°C and ' $\text{MoW}_2\text{Cl}_{12}$ ' (10.53 g; 11.84 mmol) added over a period of 30 min, after which time the reaction was allowed to warm to room temperature. After stirring for 24 hr, the yellow-brown solution was filtered from the grey precipitate

of lithium chloride and the solvent removed under vacuum. The residue was then dissolved in boiling hexane (100 mL) filtered, and the solvent removed from the filtrate to give a dark brown solid.

Vacuum sublimation (10^{-2} mm Hg) of the brown residue gave a trace of the purple compound $\text{Mo}(\text{NMe}_2)_4$ at 50°C and at $100\text{--}120^\circ\text{C}$ an orange solid sublimed (1.18 g). The mass spectrum of the orange solid showed in addition to ions derived from $\text{Mo}_2(\text{NMe}_2)_6$ and $\text{W}_2(\text{NMe}_2)_6$, several ions attributable to MoW-containing species, most notably $\text{MoW}(\text{NMe}_2)_6^+$.

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